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EXPERIMENTAL INVESTIGATION OF DIFFERENT CHEMICAL AND PHYSICAL AGING PHENOMENA IN NITRILE BUTADIENE RUBBER

Bachelor Thesis

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Experimental investigation of different chemical and physical aging phenomena in Nitrile Butadiene Rubber

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Institut für Mechanik

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Institut für MECHANIK

FAKULTÄT FÜR LUFT- UND RAUMFAHRTTECHNIK

Statutory declaration

Hereby, I declare, Alex Ferreres Pons, that I have independently written the present work, duly marked the quotations and used no sources and aids other than those indicated in the bibliography.

Neubiberg, 26.02.2018

Alex Ferreres Pons

Gratitude

First of all, I would like to thank the department team of the Fakultät für Luft- und Raumfahrttechnikof, in the Universität der Bundeswehr München, who contributed decisively to the development of this project. I thank those responsible for my work, Herr Alexander Li-on and Herr Michael Johlitz, the professors who supervised my thesis since the beginning.

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Index

Nomenclature

Character	Meaning
NBR	Acrylonitrile Butadiene Rubber
ACN	Acrylonitrile
DSC	Differential Scanning Calorimetry
NR	Natural Rubber
IR	Isoprene Rubber
SBR	Styrene Butadiene Rubber
IIR	Butyl Rubber or Isobutylene-isoprene Rubber
CR	Chloroprene Rubber
EPM	Ethylene Propylene Rubber; known as EPR
EPDM	Ethylene Propylene diene monomer
EVM	Ethylene Vinyl Acetate Rubber; known as EVA
FKM	Fluorinated Rubber; 80% of Fluoroelastomers
ACM	Acrylic Rubber
CM	Chlorinated Polyethylene
CSM	Chlorosulfurized Polyethylene
ECO	Epichlorohydrin Rubber
SI, Q, VMQ	Silicone
PE	Polyethylene
PP	Polypropylene

1 Introduction and objective

Acrylonitrile Butadiene Rubber, NBR for short, has a wide range of uses in various applications branches of the industry. This is due to its excellent oil, grease, and fuel resistance and favourable mechanical properties with good heat and aging resistance. In the field of sealing technology, for example, NBR occurs in the form of O-rings, flat gaskets or shaft seals. In various applications, Elastomers can come into contact with various media. Depending on the chemical composition these can be absorbed by the material due to diffusion and change its physical and chemical properties. The latter change is also called chemical aging, since the changes of the molecular structure and the cross-linking within the material are irreversible. These changes influence a variety of properties such as weight, tensile and flexural strength. The compatibility between the material and the medium depends mainly on the mediums polarity. However, other factors, such as the temperature or the elastomer additives added and its Acrylonitrile content, play also a role. To estimate the lifetime of NBR elements under certain environmental conditions, the occurring diffusion and aging processes must be known and understood. It is therefore essential investigate these behaviour experimentally.

In this contribution two particular experiments are pursued. First the change of mass and density of NBR due to the diffusion of IRM 903 Oil is investigated by the Archimedes principle. Secondly the influence of ageing time and temperature on the chemical ageing of NBR in ambient air is investigated by DSC experiments.

2 Theoretical basic concepts

2.1 Elastomer

An elastomer [1] [2] is a type of polymer with the characteristic of viscoelasticity, which means that it has both viscosity and elasticity. Moreover, they have very weak inter-molecular forces, generally having low Young's modulus and high failure strain compared with other materials. The term elastomer [3], which is derived from elastic polymer, is often used inter-changeably with the term rubber, although the latter is preferred when referring to vulcanizes. Each of the monomers which link to form the polymer is usually made of carbon, hydrogen, oxygen or silicon. Elastomers are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. At ambient temperatures, rubbers are thus relatively soft ($E \approx 3$ MPa) and deformable. Their primary uses are for seals, adhesives and molded flexible parts. Application areas for different types of rubber are manifold and cover segments as diverse as tires, shoe soles, and damping and insulating elements.

Elastomers are usually thermosets, requiring vulcanization, but may also be thermoplastic. The elasticity is derived from the ability of the long chains to reconfigure themselves to distribute an applied stress. The covalent cross-linkages ensure that the elastomer will return to its original configuration when the stress is removed. As a result of this extreme flexibility, elastomers can reversibly extend from 5–700%, depending on the specific material. Without the cross-linkages or with short, uneasily reconfigured chains, the applied stress would result in a permanent deformation.

The elastomers are classified in two according to his behaviour over high temperatures. They can be thermoset or thermoplastic. Thermoset elastomers do not show a change of shape and they are still solids when they are heated until, above a certain temperature, they are degraded. Most of the elastomers belong to this group. Thermoset plastic polymers (Figure 2.1) characterised by rigid, three-dimensional structures and high molecular weight, stay out of shape when deformed and undergo permanent or plastic deformation under load, and normally decompose before melting.

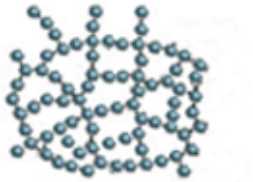


Figure 2.1: Thermoset Elastomer structure

Thermoplastic elastomers (Figure 2.2) are mouldable when increasing the temperature. Their properties change if they melt and they are moulded several times. This type of material is relatively recent, synthesized the first in 1959.

Figure 2.2: Thermoplastic Elastomer structure

Using the laws of thermodynamics, the definitions of tension and the characteristics of polymers, we arrive at an ideal behaviour of tension:

$$\sigma = nkT[\lambda_1^2 + \lambda_1^{-1}] \qquad (1)$$

Where n is the number of monomers per unit of volume, k is the Boltzmann's constant, T is the Temperature and λ_1 is the distortion in the direction 1.

These values are quite accurate up to approximately 400% deformation. At this point, the alignment between stretched chains begins to cause crystallization. While the Young's modulus does not exist for elastomers due to the non-linear nature of the stress-strain relationship, a secant modulus can be found at a particular voltage.

2.2 Aging of polymeric materials

Aging is a slow and irreversible alteration of a material chemical or physical structure. This alteration has normally a detrimental effect on the material properties. It leads to gradual loss of the design function and ultimate failure or unacceptable loss of efficiency. We are talking about the two types of aging found in the material, chemical and physical aging.

In chemical aging, we find the most important mechanism responsible for the aging of polymeric material, the chain scission. It will leads to a significant deterioration of the mechanical properties. Figure 2.3 and Figure 2.4 show the examples of anaerobic thermolyse of PE and PP.

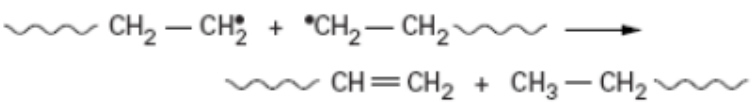


Figure 2.3: Anaerobic thermolyse of PE. [4]

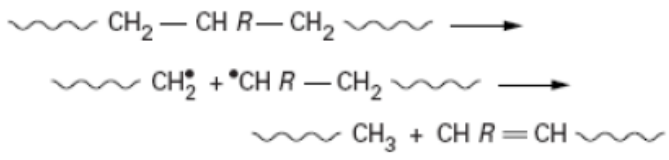


Figure 2.4: Anaerobic thermolyse of PP. [4]

It can be quantified by molecular mass measurement:

$$n(t) = \frac{1}{M_n(t)} - \frac{1}{M_{no}} \qquad (2)$$

The random chain scission has an effect on the mechanical properties. [4] The reduction of the molecular mass induced by chain scission lowers the mechanical strength and lead to embrittlement. Figure 2.5 shows this behaviour.

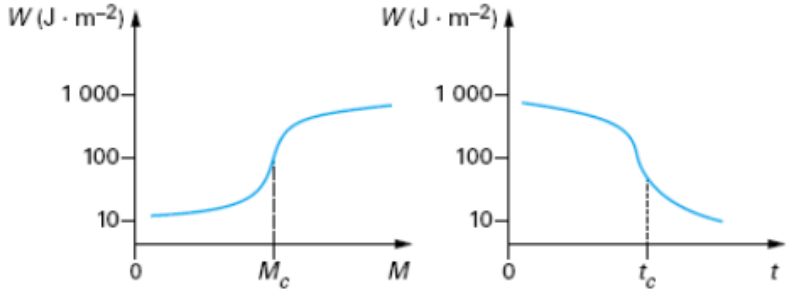


Figure 2.5: in the graph W/M it is shown that, with the reduction of the molecular mass, the mechanical strength is lower. The second graph W/t shows the behaviour over the time, where the mass is decreased and, therefore, the mechanical strength is lower.

Physical aging refers to structural relaxation of the glassy state toward the metastable equilibrium amorphous state, and it is accompanied by changes in almost all physical properties. These changes, which must be taken into account in the design, manufacture, and use of glassy polymer materials and devices, present a daunting challenge to theorists.

2.3 Diffusion

Diffusion describes the particle transport in fluids or solids, which is caused by a concentration gradient. This is due to the irregular thermal movement of the individual particles, which can be either molecules, ions or atoms. The transport takes place in the direction of the concentration gradient, i.e. in the direction smaller concentrations, through intermolecular and intramolecular spaces. [5] In 1855 Adolf Fick realized that the diffusion process was mathematically analogous to the heat conduction described by the Fourier's law (1822). [6] The first Fick's law (3) deduced from this states that the diffusion flux J of a substance, which repre-

sents the amount of the diffusing particles through unit area per unit time is directly proportional to the concentration gradient. [7]

$$J = -D\frac{\partial c}{\partial x} \tag{3}$$

D is the diffusion coefficient, *c* the concentration, *x* the distance and *∂c / ∂x* the concentration gradient along the x-axis. The law only applies to stationary processes, so those in which the concentration does not change over the time. The second Fick's law (4), however, describes the transient process, i.e. the case in which the diffusing component accumulates over time in a determined volume element of the considered system. [8]

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{4}$$

Both equations are valid on the assumption that the diffusion coefficient at constant temperature and constant pressure is independent of concentration. In fact, however, *D* mostly depends on the concentration of the diffusing substance. Thus, often only the average diffusion coefficient can often be calculated. [7], [9]

In order to calculate *D* from experimental data, explicit solutions of Fick's second law have been determined for special cases of diffusion. For example, equation (5) describes diffusion in the case of thin polymer membranes that are completely submerged in the diffusing medium. [10] The simplification here is that the diffusion takes place only in the x-direction. It is therefore considered only the mass transfer of the faces. The diffusion at the negligibly small side surfaces is not included in the calculations. With sufficiently thin plates, this relationship can be used to a good approximation if the thickness *h* of the sample is known. Formally, however, it only applies to concentration-dependent diffusion coefficients.

$$\frac{m_t - m_0}{m_\infty - m_0} = \frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\left(\frac{1}{(2n+1)^2}\right)\cdot e^{\frac{-(2\pi+1)^2\pi^2 Dt}{h^2}} \tag{5}$$

Here, m_t is the mass of the sample at time *t*, m_0 the sample initial mass, m_∞ the mass of the sample in the saturation state and *D* the diffusion coefficient. Accordingly, M_t and M_∞ are the mass increase at time *t* and in the saturation state, respectively. *n* indicates the number of summands. Experimentally, therefore, the sample mass must be continuously determined as a function of time. This is realized by sorption experiments. If a diffusion process in a polymer of the above equation obeys Fick's diffusion. In this case, the rate of mass transport is much smaller than that of the chain relaxation of the macromolecules. If the other extreme occurs, in which the relaxation proceeds much more slowly than the diffusion, then there is non-Fick's diffusion. If the velocities of both processes are comparable, one speaks of pseudo-Fick or anomalous diffusion. [8]

Furthermore, an explicit solution is also known in the case of unilaterally limited diffusion with a constant concentration of the diffusing medium on the material surface. The medium can be both a gas and a liquid which penetrates into the solid. Equation (6) represents the formulaic context. [11]

$$c(x,t) = c_s - (c_s - c_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (6)$$

Here, $c\,(x, t)$ is the concentration in the material at the distance x at time t, c_s the concentration at the surface in the equilibrium state and c_0 the initial concentration of the diffusing substance in the interior of the material interior. If it is ensured that a substance only penetrates on one side, with sufficient substance present to ensure a largely constant concentration of medium, the diffusion coefficient can also be calculated from the above equation. In this case, however, the concentration profile of the diffusing component in the solid must be determined for a specific diffusion time. Thus, the local resolution of the content of a substance is needed for calculations. [11]

Figure 2.6 shows the relationship between the course of the concentration profile and D, t and c_s. [12]

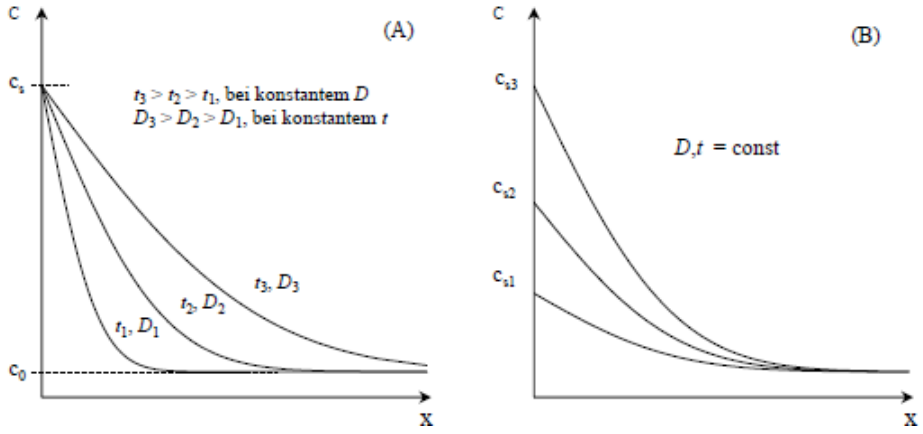


Figure 2.6: (A) dependence of the concentration c *on the penetration depth* x *for a particular material-medium combination at different diffusion coefficients or times in the case of a constant surface concentration; (B) dependence of the concentration* c *on the penetration depth* x *for substances with different* c_s *at the same D and t; the concentration of the medium is constant*

For elastomers, depending on the source potential of a substance or the absorption behaviour of a medium at different concentrations of the medium, different equilibrium surface concentrations c_s on the material surface can be established (compare Figure 2.6 (B)). The curve is flatter, the larger the diffusion coefficient (at t = constant) or the longer the duration of the diffusion (at D = constant) (see Figure 2.6 (A)).

Furthermore, an explicit solution is known for the case in which a limited amount of a substance diffuses. This is, for example, given when a drop of a compound is applied to a piece of polymer. The surface concentration and the course of the concentration change with the time course of the diffusion process. Equation (7) describes this process.

$$c(x,t) = \frac{N}{\sqrt{\pi D t}} \cdot e^{\left(-\frac{x^2}{4Dt}\right)} \qquad (7)$$

Here, *c (x, t)* is the concentration of the diffusing substance at time *t* at location *x*, *N* is the constant amount of diffusing medium per unit volume, and *D* is the diffusion coefficient. Figure 2.7 shows qualitative concentration curves for the case of diffusion, with limited medium concentration as a function of the diffusion time and the diffusion coefficient. It is assumed that the same amount of substance diffuses in each case.

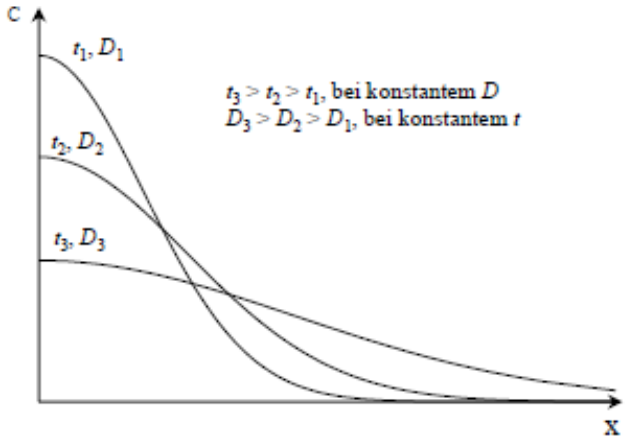


Figure 2.7: Dependence of the concentration on the penetration depth for different diffusion times or diffusion coefficients; the amount of diffusing substance is the same.

The concentration profiles show a sigmoidal curve, which becomes flatter with increasing diffusion time (at constant *D*) or with increasing diffusion coefficient (at constant *t*). As the substance migrates into the interior of the material, the content of the surface simultaneously decreases. This happens until a constant concentration has set in the entire material.

2.4 Archimedes' principle

Archimedes' principle states that the upward buoyant force that is exerted on a body immersed in a fluid, whether fully or partially submerged, is equal to the weight of the fluid that the body displaces and acts in the upward direction at the centre of mass of the displaced fluid.

2 Theoretical basic concepts

Archimedes' principle is a law of physics fundamental to fluid mechanics, formulated by Archimedes of Syracuse. In *On Floating Bodies*, Archimedes suggested that (c. 250 BC):

- *Any object, wholly or partially immersed in a stationary fluid, is buoyed up by a force equal to the weight of the fluid displaced by the object* (250BC). [13]

Consider a cube immersed in a fluid, with its sides parallel to the net direction of gravity. The fluid will exert a normal force on each face, and therefore only the forces on the top and bottom faces will contribute to buoyancy. The pressure difference between the bottom and the top face is directly proportional to the height (difference in depth). Multiplying the pressure difference by the area of a face gives the net force on the cube – the buoyancy, or the weight of the fluid displaced. By extending this reasoning to irregular shapes, we can see that, whatever the shape of the submerged body, the buoyant force is equal to the weight of the fluid displaced. The principle of Archimedes is formulated as follows:

$$E = P_e V = \rho_f g V \qquad (8)$$

Or when one want to determine it to compare against the weight of the object:

$$E = -P_e V = -\rho_f g V \qquad (9)$$

where E is the buoyancy [N], P_e is the specific weight of the fluid [N / m^3] ρ_f is the density of the fluid, V the volume of fluid displaced by some body submerged partially or totally in the same, g the acceleration of gravity and m the mass.

Although the Archimedes' Principle was introduced as a principle, in fact a demonstrable theorem can be considered from the Navier-Stokes equations for a fluid at rest. [14] [15] [16] Using the Stokes theorem, but also the principle of Archimedes can be deduced mathematically from Euler's equations for a fluid at rest, which in turn can be deduced by generalizing Newton's laws to a continuous medium. Starting from the Navier-Stokes equations for a fluid:

$$\rho_f \left[\frac{\partial y}{\partial x} + v(\nabla \cdot v)\right] = \mu \Delta p + \rho_f g \qquad (10)$$

The mass and the volume of the body are determined. With the hydrostatic balance (see Figure 2.8), the body is weighed once in air, and then, in a liquid of known density.

2 Theoretical basic concepts

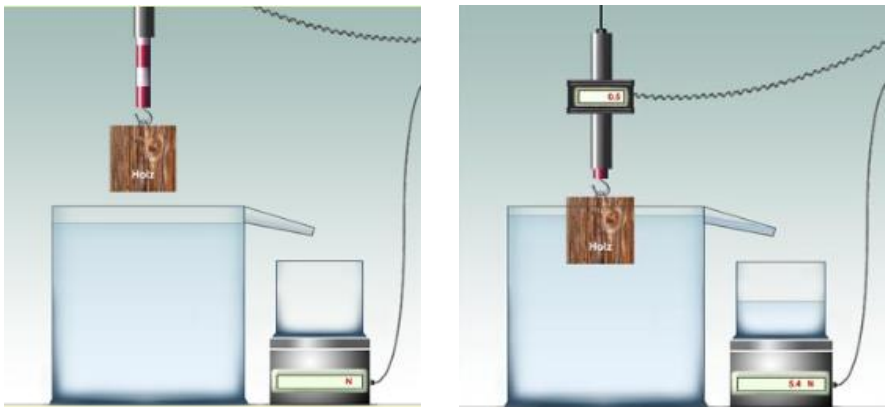


Figure 2.8: Hydrostatic balance

The first weighing m_A (mass in air) gives the mass of the body. From the display of the balance at the second weighing m_L (mass in liquid, water in that case), the volume of the body can be calculated. [17] The difference between m_A-m_L, the apparent lost mass, is the mass of the displaced liquid. That mass divided by the density of the liquid results in the volume of the displaced liquid and therefore, the volume of the submerged body.

$$V(body) = \frac{m_A - m_L}{\rho(liquid)} \tag{11}$$

Where m_A is the mass of the body in air, m_L the mass of the body submerged in the liquid and *ρ(liquid)* the density of the liquid. To select the density for the liquid, we chose the correspondent for the room temperature (23,6°C) at the moment of doing the tests. In Table C.1, it can be found a table to select the density of our liquid.

For the density of the body we have the following equation:

$$\rho(body) = \frac{m(body)}{V(body)} \tag{12}$$

And it is known that *m(body)* means the same as m_A. Then, replacing in the equation (12) the term *V(body)* for the equation (11), we have that:

$$\rho(body) = \frac{m_A}{\frac{m_A - m_L}{\rho(liquid)}} = \frac{m_A \cdot \rho(liquid)}{m_A - m_L} \tag{13}$$

3 Diffusion of oil in Acrylonitrile-Butadiene Rubber

3.1 Materials

3.1.1 Acrylonitrile-Butadiene Rubber (NBR)

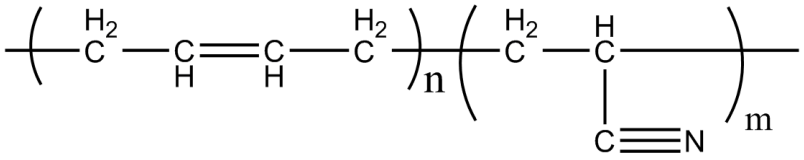


*Figure **3.1**: Structure of Acrylonitrile-Butadiene Rubber (NBR)*

Nitrile rubber, also known as Buna-N, Perbunan, acrylonitrile butadiene rubber, and NBR, is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene. Nitrile butadiene rubber (NBR) is family a of unsaturated copolymers of 2-propenenitrile and various butadiene monomers (1,2-butadiene and 1,3-butadiene) (see Figure 3.1). Although its physical and chemical properties vary depending on the polymer's composition of nitrile, this form of synthetic rubber is unusual in being generally resistant to oil, fuel, and other chemicals (the more nitrile within the polymer, the higher the resistance to oils but the lower the flexibility of the material). NBR products are established standard elastomers for special technical applications because of their good mechanical properties and good aging and abrasion resistance. Due to their good resistance to aliphatic hydrocarbons and other non-polar media, they have a very wide range of applications. It is used in the automotive and aeronautical industry to make fuel and oil handling hoses, seals, grommets, and self-sealing fuel tanks, since ordinary rubbers cannot be used. It is used in the nuclear industry to make protective gloves. NBR's ability to withstand a range of temperatures from −40 to 108 °C (−40 to 226 °F) makes it an ideal material for aeronautical applications. Nitrile butadiene is also used to create moulded goods, footwear, adhesives, sealants, sponges, expanded foams, and floor mats.

Vulcanizes made of nitrile rubber have a favourable aging behaviour, low abrasion and a high resistance to oils, fats and hydrocarbons. The content of acrylonitrile in NBR can be between 18 and 50 percent and influences the following properties:

- Resistance to swelling
- Elasticity
- Flexibility at low temperatures
- Gas permeability
- Hardening by compression

3 Diffusion of oil in Acrylonitrile-Butadiene Rubber

NBR concoctions with low acrylonitrile (ACN) content have good low-temperature flexibility. Conversely, higher ACN levels indicate a worse cryogenic flexibility increases fuel and oil resistance. Furthermore, the elasticity decreases with increasing ACN content and the compression set, or hardening by compression, increases. The thermal range of application varies depending on the composition of the mix and plasticizer content from -55°C to +100°C. It should be remembered that the elastomer hardens at higher temperatures.

The both series of tested samples of NBR1 consisted of 18% acrylonitrile (ACN) content. The total composition of the NBR1 is described in Table 3.1. Samples used in first series (Material 1) were the original samples of NBR, whereas samples used in second series (Material 2) were extracted. The extraction was performed in a Soxhlet extractor using acetone (purest) for 5 days. In the sorption experiments were used thinner specimens (30 mm × 10 mm × 1 mm) with average mass of 0,3198 g (it is necessary to add the average mass)nevertheless, different properties in its composure.

	NBR 1
ACN content %	18
Polymer	100
Filler (carbon black N 550)	60
Plasticizer (DEHP)	20
Antioxidant (6-PPD)	2
ZnO	5
Stearic acid	1
CBS	1,5
TMTM-80	0,5

Table 3.1: Composition of the NBR1 elastomers

3.1.2 Oil IRM 903

For the storage of the elastomer samples in the experiment, was used the reference oil IRM 903, listed in DIN ISO 1817. [18] It can be classified different types of oil depending on the swelling capacity. IRM 901 is categorized as a 'low swelling', IRM 902 as a 'medium swelling' and IRM 903 as a 'high swelling' oil. The three reference oils are petroleum products that must evince predetermined properties. They are representative of low-alloyed mineral oils. Table 3.2 shows the specifications and typical properties of the oil. Solidification point, refractive index and aromatic content cannot be guaranteed by the suppliers, according to the standard. [18] The oil IRM 903 used was acquired for Institute of Mechanics from the Fuchs Schmierstoffe GmbH, Mannheim/Deutschland.

	Conditions	
Specifications	IRM 903	Test methods
Aniline point	70±1	ISO 2977
Kinematic viscosity	33±1[a)]	ISO 3104
Flashpoint ºC min	163	ISO 2592
Density at 15ºC g/cm^3	0,921±0,006	ISO 3675
Naphthene content, c_N, %	≥ 40	
Paraffin content, c_P, %	≤ 45	
Typical properties		
Freezing point ºC	-31	ISO 3016
Index of refraction at 20ºC	1,5026	ISO 5661
Aromatic content c_A %	14	

Table 3.2: Specification and typical properties of reference oil according to DIN ISO 1817 [18]

[a)] measured at 37,8ºC

3.2 Preparation

Original unaged samples were used to determine changes of material properties during aging time in dependence on increasing temperature and reaction with reference oil. The strips, approximately 30 x 10 x 0,1 mm, of Material 1 and Material 2 were stored for a certain time and temperature. Accelerated thermal aging of the strips was carried out in temperature controlled (with sensitivity of ±1°C), commercial air-circulating ovens TR60 from NABERTHERM at 60°C, 80°C, 100°C and 120°C. The duration of the thermal aging was up to 365 and 197 hours, for Material 1 and Material 2 respectively. For each temperature were applied 3 samples of the material to obtain a precise result.

The Material 2 was prepared by extraction from Material 1 using Soxhlet apparatus. It is assumed that from Material 2 was extracted almost completely plasticizer (DEHP) and antioxidant (6-PPD) as well.

Before the start of experiments mass and size were measured for all unaged samples. Figure 3.2 shows the sample geometry, as well as Table 3.3 displays the measured size values of original samples. Weight was measured with an analytical balance CPA223S from SARTORIUS. This mass measurement was carried out before the aging process as well as after definite aging time. Afterwards for the density measurements were applied Archimedes principle. Figure 3.3 shows the density measurements. The weight for determination of sample density was obtained hanging the samples below the analytical scales, submerging each sample in distilled water (approx. 500 ml). This way, with the Archimedes Theorem [19], it is possible to know the physical properties of the samples. The density was defined using the equation (13).

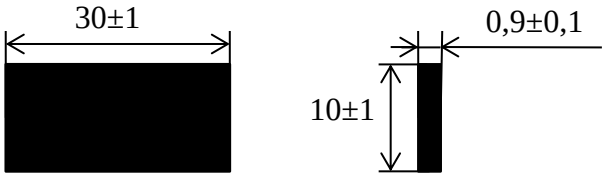
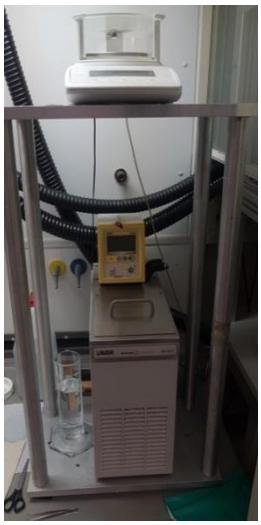


Figure 3.2: Sample geometry

3 Diffusion of oil in Acrylonitrile-Butadiene Rubber

(A)

(B)



(C)

Figure 3.3: Material used in the diffusion tests. (A) Test tube with distilled water (B) Balance to weigh the mass in air (C) balance with the mechanism to measure the weight in the liquid

	Material 1			*Material 2*		
Sample number	length (mm)	width (mm)	thickness (mm)	length (mm)	width (mm)	thickness (mm)
1903601	31,36	9,75	0,91	30,25	8,49	1,25
1903602	31,05	9,88	1,17	29,38	6,21	1,23
1903603	30,19	9,74	0,92	30,06	9,05	0,82
1903801	31,08	11,14	0,96	28,96	9,00	0,82
1903802	30,34	9,85	0,98	29,39	8,42	1,00
1903803	30,31	10,96	0,87	28,69	9,31	0,88
19031001	30,98	9,65	0,97	25,00	9,30	0,92
19031002	30,15	11,38	0,91	26,90	9,29	0,93
19031003	30,23	9,73	0,94	28,41	9,30	0,80
19031201	31,81	11,25	0,92	29,41	9,30	1,14
19031202	29,46	10,81	0,91	29,66	9,28	1,00
19031203	30,70	10,69	0,93	27,44	9,37	1,02

Table 3.3: Size values of the unaged samples

The each sample was stored with the reference oil IRM 903 into the glass with the cover. The oil diffusion into the material should be realized through the whole surface of specimen. In consequence of this important fact, the surface should not be in contact with the glass wall, which means the all surfaces should be free. At this point the metallic net with adjusted form was needed, to keep the samples in suspension. Once the nets were placed in those glasses, they were filled with oil and after that the samples were submerged into the medium. Considering the oil is high swelling, the glasses were made full up to 1,5 cm under glass edge. In Figure 3.4 (A-D) is shown the net form and the following steps of storing the samples.

Glasses were marked with numbers, which note the material of the rubber, the type of oil and the corresponding temperature. For each temperature were used 3 samples for the sake of statistic.

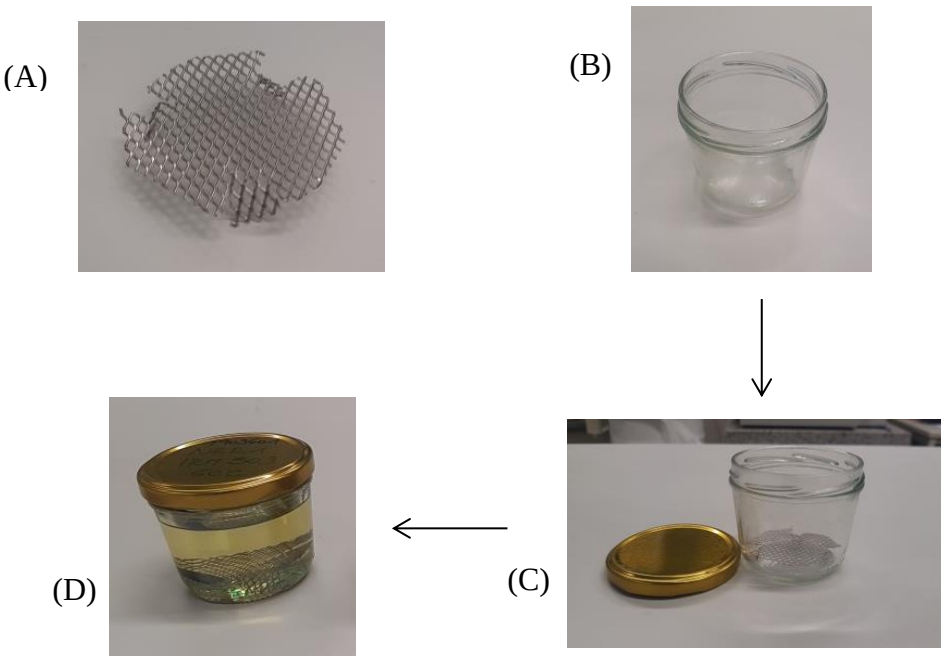


Figure 3.4: Steps followed for the preparation of the samples

3.3 Weight and density measurement

Weighting should be quite quick and accurate to achieve the most precise results at the end. The first few days the samples were measured every hour after storing into the medium in air-circulating oven. After 79 hours of aging time the frequency of measurement was changed to every 4 hours.

In order to determine the increase in mass of the elastomers, they were regularly taken from the medium, cleaned with technical benzene and weighed with the analytical scales CPA223S from Sartorius, with sensitivity of ±0.5 mg. This procedure was repeated until no significant

mass change was detected. Since the time between weighing was much greater than the actual weighing operations, errors resulting from non-immersion of the elastomer in the aging medium can be neglected. [21]

Last step, like was explained before, is to take out the samples from the water, dry them, and get them in again in the glasses again.

3.4 Results

3.4.1 Original NBR 1

The Material 1 provided the first week was tested many weeks with a range of long periods of hours to see the behaviour of our material in reaction with the oil increasing the temperature, which simulates the working temperature the rubber is used to deal with. As we can see in Figure 3.5, the colour of the oil changes differently over the hours depending on the working temperature. The looking of our liquid varies more at higher temperatures.

Figure 3.5: Difference between colours of the oil in some Temperatures. From left to right, T= 60°C, 80°C, 100°C and 120°C

The important fact to analyse is the variation of the mass over the time, and the variation of the body density over the time. The calculus of the last one was realised with the equation (13) shown in the last chapter. Figure 3.6 and Figure 3.7 show the plots of the mass and the density variations over the time, to understand the behaviour of the material.

3 Diffusion of oil in Acrylonitrile-Butadiene Rubber

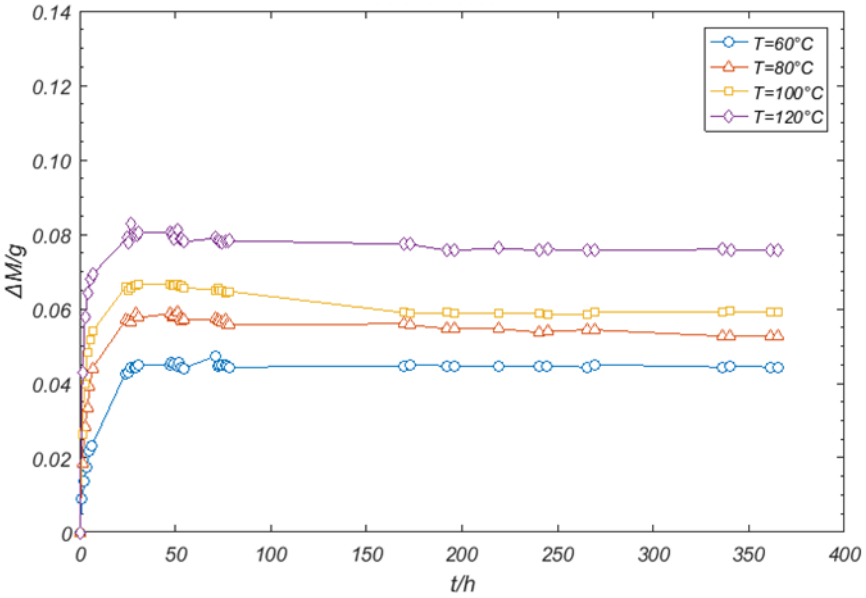


Figure 3.6: Variation of the Mass over the time

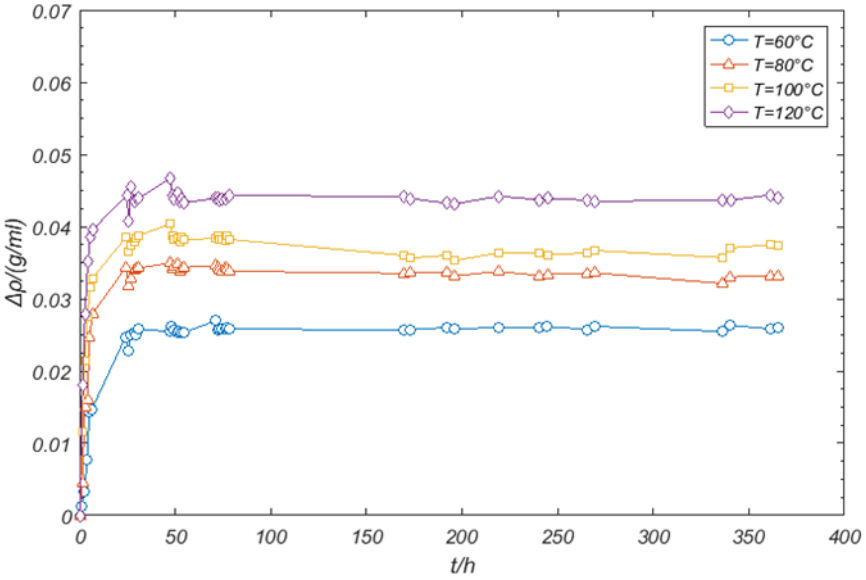


Figure 3.7: Variation of the Density over the time

By looking the graphs, we notice the experimental changes of properties that it was explained in the theory. It is important to say that, as it was commented in Chapter 3.2, the results are the average of three samples for each temperature. Then, in graphs, it is only shown this average to analyse every temperature. As we can see, the mass and density represented as variation of them, to start from zero in the unaged time, increase in the first hours. In the next hours, approximately in the second day of work, these properties maintains constant over the time. Remember that density depends directly on mass so if this does not change, density is constant too. Have a look to Figure 3.8 and Figure 3.9 to see the plots with the time in a logarithmic scale.

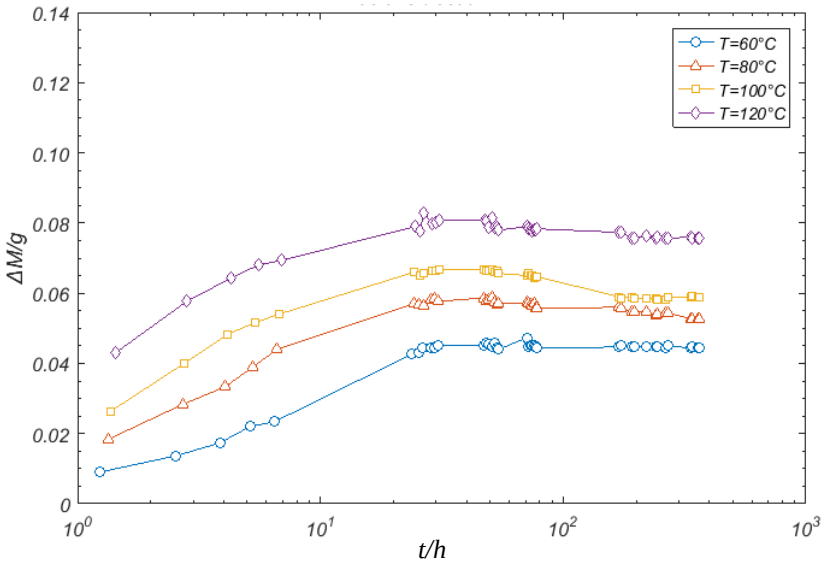


Figure 3.8: Variation of the Mass over the time, with x-axis in logarithmic scale

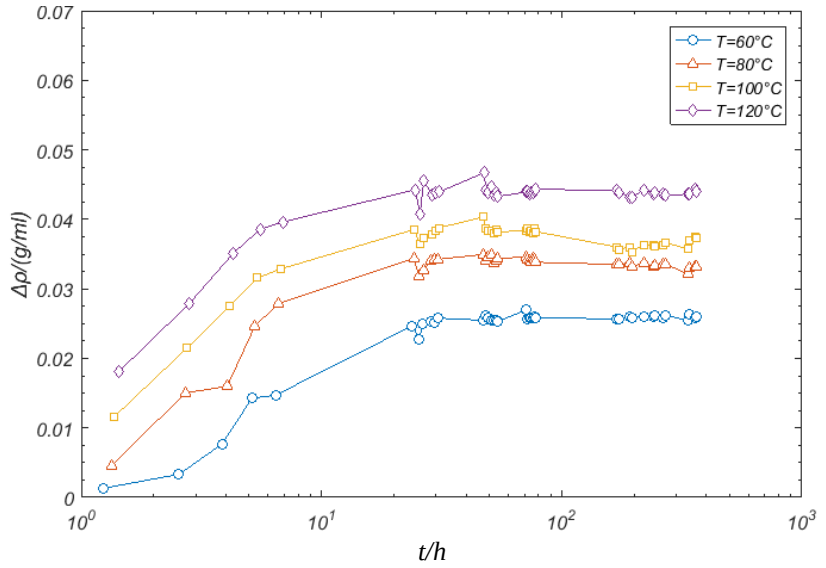


Figure 3.9: Variation of the Mass over the time, with x-axis in logarithmic scale

3.4.2 Extracted NBR 1

This material was provided the second week of tests, while we started essaying with Material 1 only every 4 hours. The process was the same as the first, with the difference of composition of the rubber, which did not affect us in the testing. There were no notable variations between Material 1 and 2 doing the experiments and calculus, and it must be added that with no longer time, it was unlikely to analyse changes in the rubber's composition. As the other rubber, we had a few weeks to work with the material, with a range of long periods of hours to see the behaviour in reaction with the oil increasing the temperature.

3 Diffusion of oil in Acrylonitrile-Butadiene Rubber

The important fact to analyse is the variation of the mass over the time, and the variation of the body density over the time. The calculus of the last parameter was realised with the equation (13) shown in the last chapter. In Figure 3.10 and Figure 3.11, see the plots of the mass variation over the time and the density variation over the time, to understand the behaviour of the material.

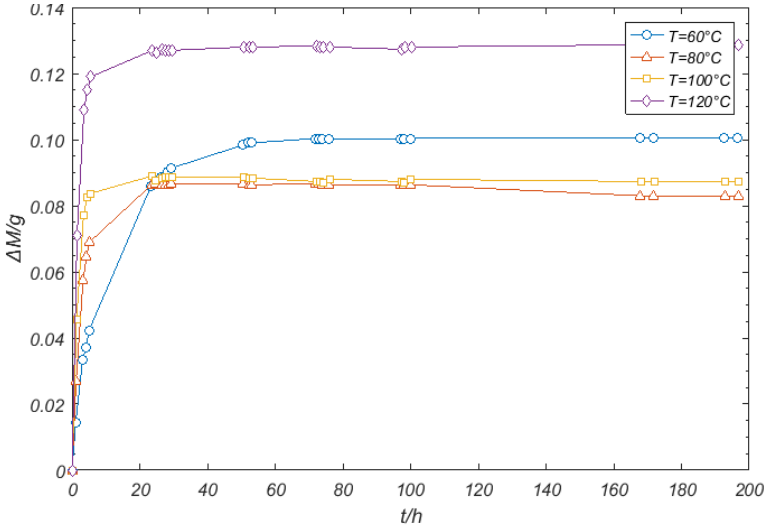


Figure 3.10: Variation of the Mass over the time in Material 2

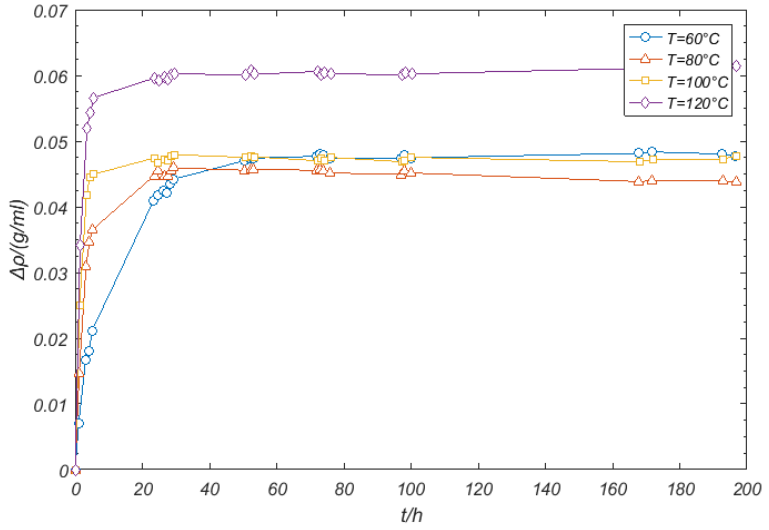


Figure 3.11: Variation of the Mass over the time in Material 2

By looking the graphs, we notice the experimental changes of properties that it was explained in the theory. It is important to say that, as it was commented in Chapter 3.2, the results are the average of three samples for each temperature, as well as the Material 1. Then, in graphs, it is only shown this average to analyse every temperature. As we can see, the mass and density represented as variation of them, to start from zero in the unaged time, increase in the first

hours. In the next hours, approximately in the second day of work, these properties maintains constant over the time. Remember that density depends directly on mass so if this does not change, density is constant too. Have a look to Figure 3.12 and Figure 3.13 to see the plots with the time in a logarithmic scale.

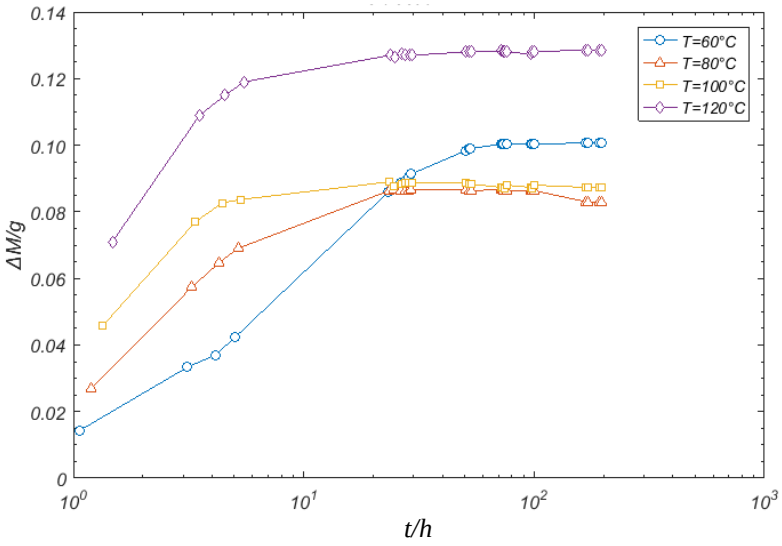


Figure 3.12: Variation of the Mass over the time, with x-axis in logarithmic scale

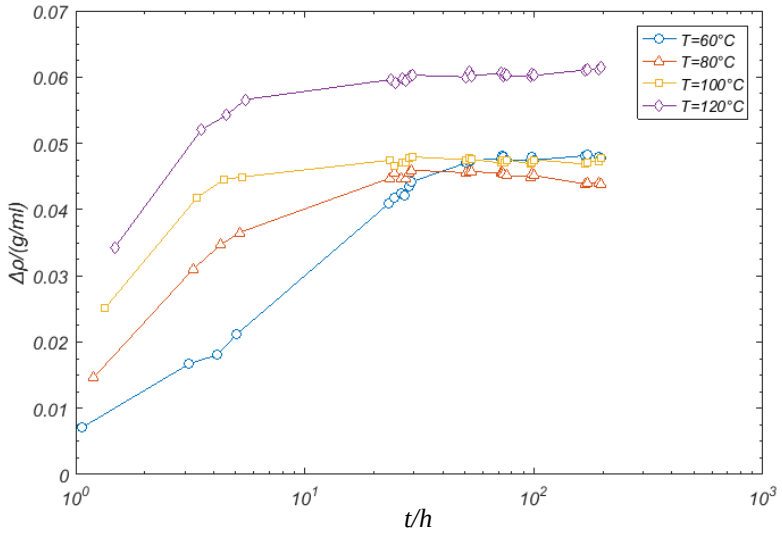


Figure 3.13: Variation of the Mass over the time, with x-axis in logarithmic scale

4 Determination of glass transition and heat capacity

4.1 The glass transition of polymers

The glass transition is a reversible transition in amorphous materials. This transition comprises a smooth increase in the viscosity of a material by as much as 17 orders of magnitude within a temperature range of 500 K without any pronounced change in material structure [21]. The consequence of this dramatic increase is a glass exhibiting solid-like mechanical properties on the timescale of practical observation. In contrast to the crystallization transition, the glass transition is a second-order phase transition in the Ehrenfest classification. It involves changes in thermodynamic and mechanical properties such as volume, energy, and viscosity. In many materials that normally undergo a freezing transition, rapid cooling will avoid crystallization and instead result in a glass transition. Other materials, such as many polymers, lack a well-defined crystalline state and easily form glasses, even upon very slow cooling or compression. The tendency for a material to form a glass while quenched is called glass forming ability. This ability depends on the composition of the material and can be predicted by the rigidity theory. [22]

Below the transition temperature range, the glassy structure does not relax in accordance with the used cooling rate. The expansion coefficient for the glassy state is roughly equivalent to that of the crystalline solid. If slower cooling rates are used the increased time for structural relaxation or intermolecular rearrangement results in a higher density glass product. Similarly, by annealing (and thus allowing for slow structural relaxation) the glass structure in time approaches an equilibrium density corresponding to the supercooled liquid at this same temperature. The glass transition temperature *Tg* is located at the intersection between the cooling curve (volume versus temperature) for the glassy state and the supercooled liquid. This temperature depends, like the process of the transition, on the used cooling rate. It is an important value for polymers, indicating the relationship between temperature and dimensional stability. For elastomers, *Tg* indicates the transition from elastic energy to elastic entropy behaviour. Its value depends on the elastomers chemistry e.g. their degree of crosslinking. The differential scanning calorimetry, from now on called DSC, is used to determine the glass transition temperature by measuring the in- and outgoing heat flow of the investigated polymer sample.

4.2 Heat capacity of Acrylonitrile-Butadiene Rubber (NBR)

In the DSC experiments the same material is investigated as in the diffusion experiment. By the measured heat flow which is caused by the temperature gradient due to the given temperature rate on the samples surface the heat capacity can be determined. The heat capacity of a body is the quotient between the amount of heat energy transferred to a body or system in any process and the temperature change it experiences.

$$C = \frac{\dot{Q}}{\dot{T}} \tag{14}$$

In a more rigorous way, it is the energy necessary to increase the temperature of a certain substance in a unit of temperature [23]. It indicates the difficulty that a body presents to undergo temperature changes under the heat supply and can be interpreted as a measure of thermal inertia. It is an extensive property, since its magnitude depends, not only on the substance, but also on the amount of matter of the body or system. In order to get an intensive value for the heat capacity *C*, the measured ingoing heat is divided by the samples mass, which leads to the specific heat capacity *c*.

$$c = \frac{C}{m} \tag{15}$$

Since the DSC measurements are executed under isobaric conditions, the ingoing heat is split in internal energy of the sample and the amount of volume dilatation work the samples surface supply to the environment. Under isochoric conditions the second part would vanish since the sample surface couldn't move. In order to distinguish between both conditions the specific heat capacity is at constant pressure called c_p and at constant volume called c_v. Since the surface of solid samples moves very little due to temperature changes, the difference between c_p and c_v of solids is at ambient pressure conditions very small. In general, the heat capacity also depends on the temperature and the pressure.

4.3 Differential Scanning Calorimetry (DSC)

Above it was already mentioned that the DSC measures the in- and outgoing heat flow of an investigated sample. In Figure 4.1 it can be seen in detail that the reference and the filled sample crucible are supplied by the same heat source. Thus the path of the heat flow splits over the low resistance metal plate into the two paths to the crucibles. By the continuous measuring of the temperature difference between the ends of both paths on the boundary to crucibles the difference of the two heat flows can be determined. This difference, from which the method's name is derived, is mainly caused by the heat flow into the sample, which is the point of interest. Within the thermal chamber also other heat flows occurs but their amount can be neglected since the resistance of those paths are very high. In practices a DSC experiment is operated by a given temperature program which includes heating, cooling and isothermal segments. The heat sources is controlled in order to follow this given temperature programme. If the sample changes its physical or chemical properties during the experiment, the control system reacts due to the temperature changes which are caused by the absorbed or given heat of the sample. This event occurs as peaks or turning points in the measured heat flow. An exothermic effect occurs when the material reacts with heat release. If the material absorbs energy, then it is spoken of an endothermic process. Since the pressure is kept constant in the experiments the measured heat flow is equal to the enthalpy rate. For this contribution, the DSC type 204 F1 Phoenix of the company Netzsch was used. In this machine only the heating process is properly adjusted. Thus the heating process is used to determine the specific enthalpy rate which gives feedback of the material's state.

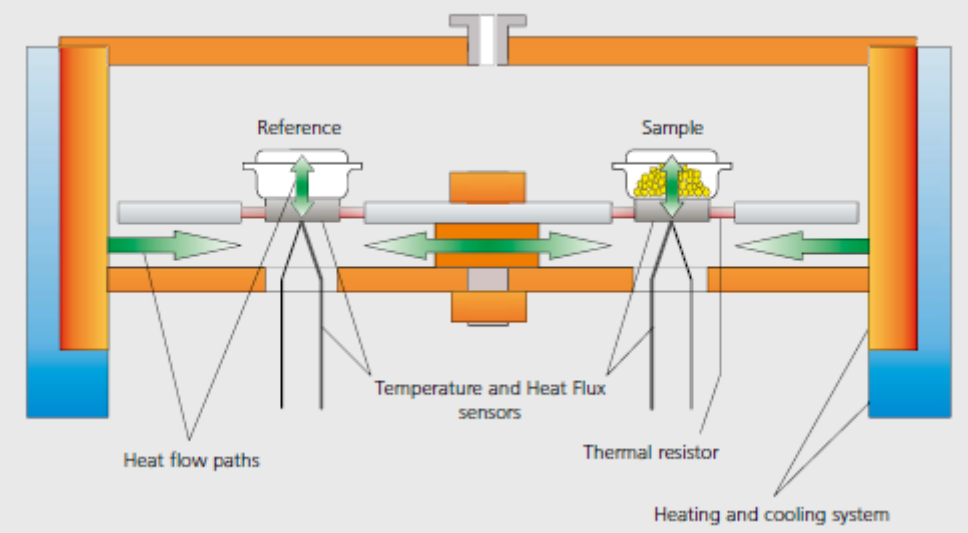


Figure 4.1: DSC measuring principle

4.4 Details and results of the experiment

Before the DSC experiments were applied on the samples, they were aged in furnaces. In Table 4.1 the therefore used temperature levels and ageing times are shown. In the DSC experiment the following temperature programme was used: From a starting temperature of 23°C the sample is cooled down to -90°C by a rate of 10 K/min in order to start the first heating process below the glass transition. The same rate is used for the following heating process up to 120°C. After a short isothermal settling phase of two minutes the sample is cooled down to -90°C again.

To get more graphs of the measured enthalpy rates during the heating processes for comparisons, this temperature cycle is repeated three times. If the graphs of the three measured enthalpy rates superposes each other it is proven that the heating process causes no chemical change in the sample. In the ageing processes before the DSC experiment on the other hand, the polymer structure of the polymer is degraded. This also influences the step in the graph of the enthalpy rate which is caused by the glass transition (see Figure 4.2, Figure 4.3, Figure 4.4). By evaluating the areas, which are spanned by the step over the time, a scalar value can be determined to characterise the current ageing state of the sample. Figure 4.4 shows the results of this evaluation for the second heating process which delivers the same graph of the enthalpy rate than the third heating process. Considering the results, it is clear that higher temperature levels accelerate the ageing process dramatically. It can be seen, that at a temperature level of 100°C the time to reach the same ageing state is four times longer than at 120°C.

		Aging Time (h)					
		4	48	168	336	1008	3024
T (°C)	120	26,23	23,87	21,91	18,23		
	100			25,81		21,74	
	80			26,34			24,19
	0	26,4	26,4	26,4	26,4	26,4	26,4

Table 4.1: Results of DSC Area (J / g) under the curve, for the aging times selected

4 Determination of glass transition and heat capacity

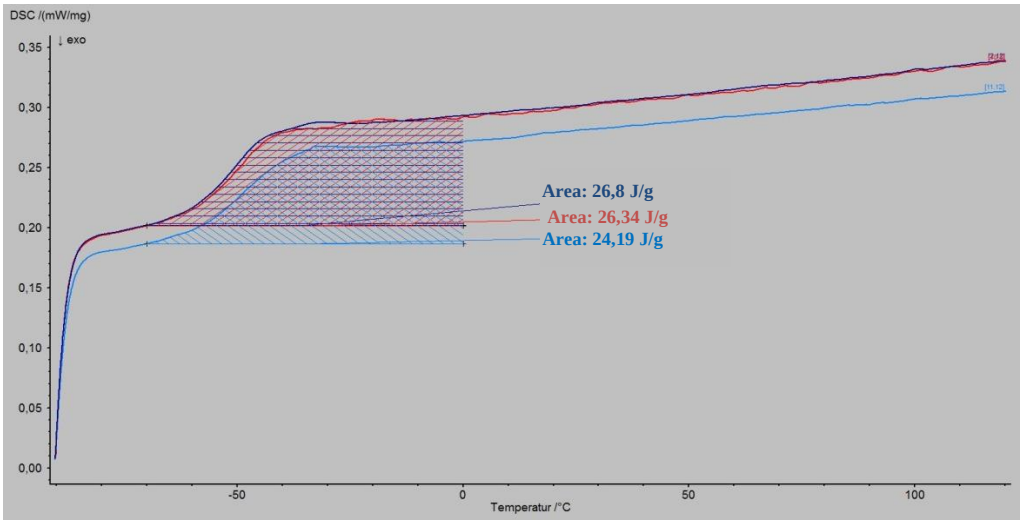


Figure 4.2: Graph of the entalphy rate, from unaged Time to 3024h, at 80°C

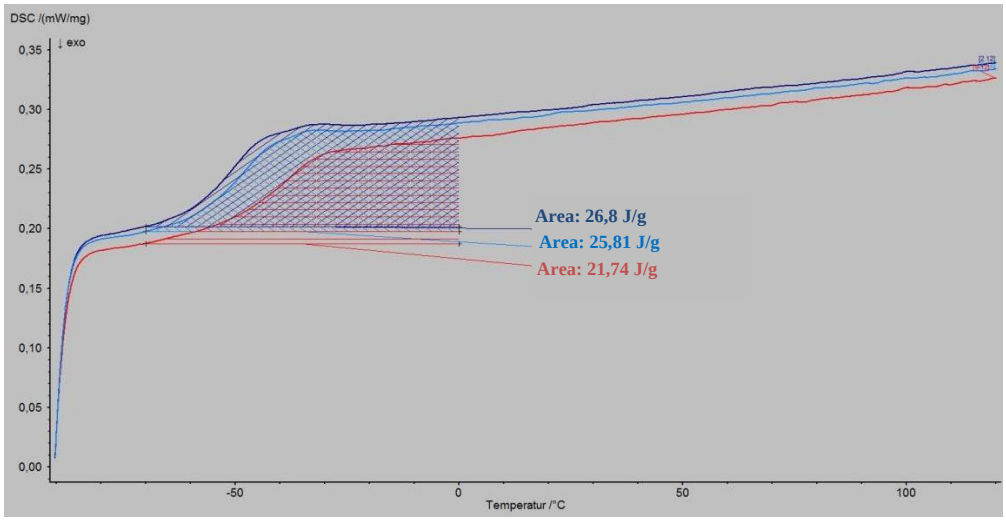


Figure 4.3: Graph of the entalphy rate, from unaged Time to 1008h, at 100°C

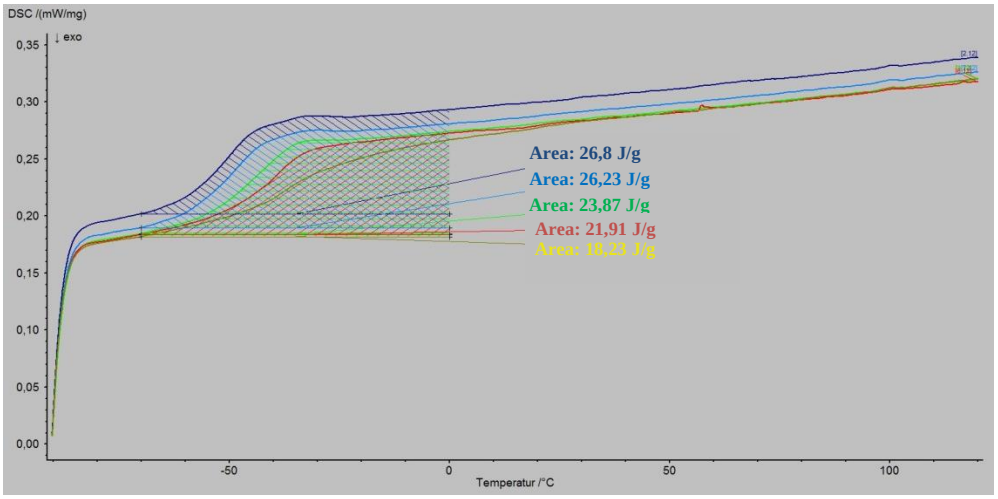


Figure 4.4: Graph of the entalphy rate, from unaged Time to 336h, at 120°C

4 Determination of glass transition and heat capacity

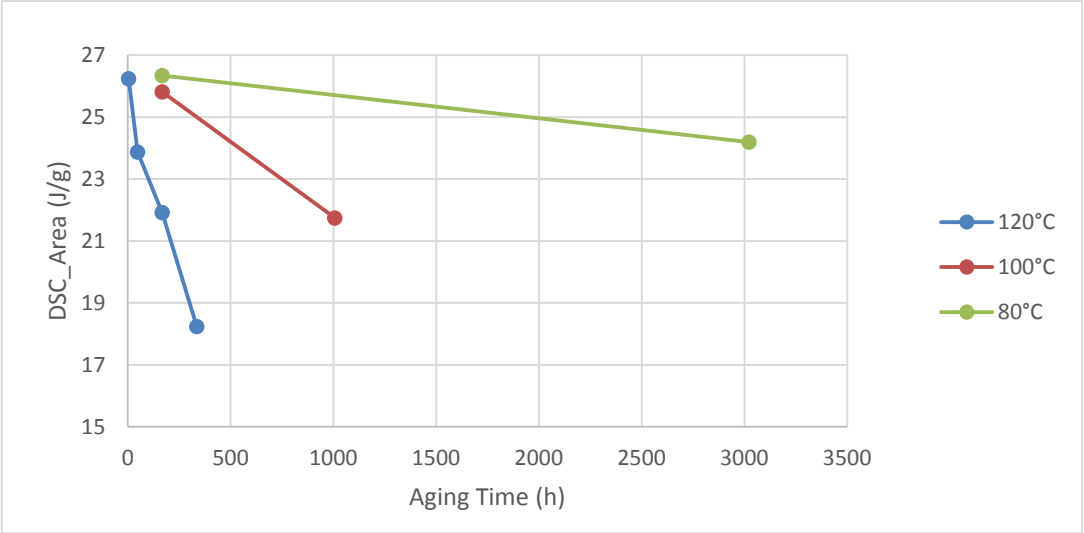


Figure 4.5: Graph with the DSC Area (J / g) obtained in the different Aging Times (h). In the Diagram B.1 it is shown a 3D plot of the correspondent points

5 Summary and Outlook

In this work, we have tested different cases that the rubber works in real situations. In the industry it is found this material in many models of machines for the assembly of the pieces and keep the junctures united. There are other situations, like in the aeronautical field or the automotive, that could be found the use of such material. In all of them, the changes of temperature and the stresses they work with are considerable. For that reason, it is one objective to make simulations in controlled essays to know how the different materials behave over the time, influenced by different parameters.

The experiments show us the different physical and chemical aging parameters in elastomers. We demonstrated that, with high temperatures, the aging time of material is considerably shorter, being affected with external factors, such as liquids, air, forces. In that work, it was not accomplished the part of work with mechanical behaviour with the parameters given and the conditions the material was involved during the labour. This was due to the fact that we did two experiments, and we had to accomplish all the goals for both experiments and the questions spoken with the professors to finish the project. With DSC essays, we found a much known property for us, the glass transition and its parameters of studying. We included the temperature of glass transition, the heat capacity, the enthalpy, the aging time, and a few more parameters useful to work with to study this field. The main objective of this experiment was to find the chemical aging of the rubber.

The next experiment done, the second chronically made along those months for the project, was the diffusion of oil in NBR. The goal of this was to study the behaviour of the composition of the rubber and its physical parameters, such as mass, density. The samples were tested placing in the ovens of different temperatures. These samples had an initial mass and volume, which were variated over the time differently depending temperature. The physical properties were different because of the samples were submerged in oil, which with the temperature was possible to diffuse in the rubber. In the real life it is an important field to study in thermodynamics. Different materials are daily subject to fluids, liquids or gaseous, which affect the material worked with.

In the arrival to the department, it was exposed different projects to do, which were being carried out by other students and professors in the team. At the beginning, I suggested to work with the DSC experiments, because of the practical realization, which I found more interesting than the more theorical essays. When I accomplished with the goals established, I was assigned to do some tests with NBR samples to essay the diffusion in oil in this material, over the time at different temperatures. The summary of all is that the objectives have been aimed, with the acquisition of experience for me, and an important improvement of the teamwork.

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7 Annex

A Pictures

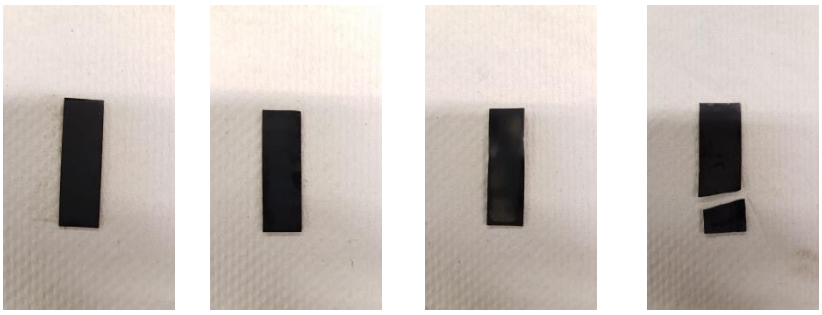

Figure A.1: Samples which we work with in the essays. Material: NBR1. From left to right: T=60°C, T=80°C, T=100°C, T=120°C. See that the more working temperature, the more rigid the material becomes. With the highest temperature, it has broken.

7 Annex

B Diagrams

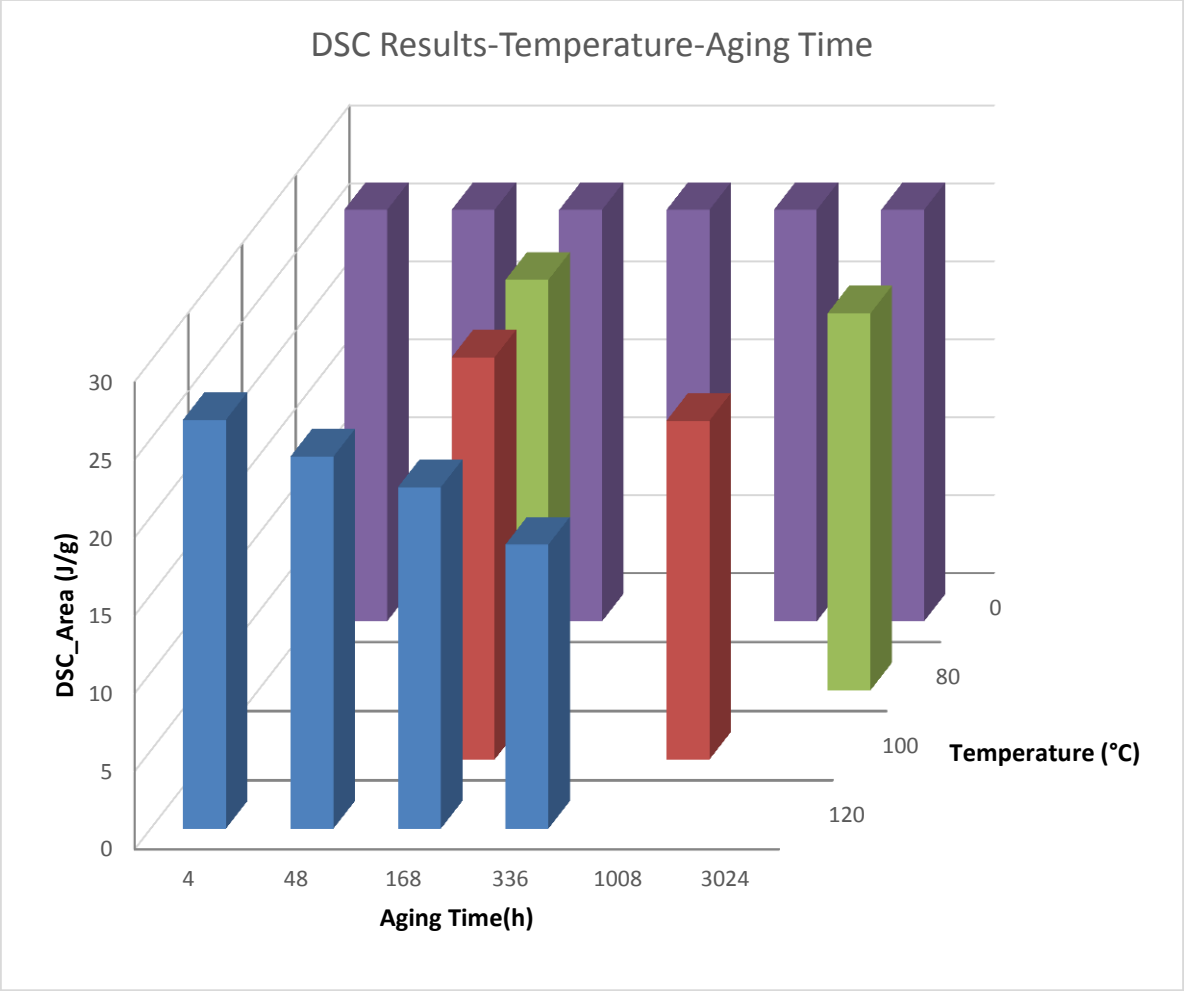

Diagram B.1: 3D Plot of DSC Area under the curves for the Aging time with the different Aging Temperatures

7 Annex

C Tables

°C	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
0	0,999843	0,99985	0,999856	0,999863	0,999869	0,999875	0,99988	0,999886	0,999892	0,999897
1	0,999902	0,999907	0,999911	0,999916	0,99992	0,999925	0,999929	0,999932	0,999936	0,99994
2	0,999943	0,999946	0,999949	0,999952	0,999955	0,999957	0,99996	0,999962	0,999964	0,999965
3	0,999967	0,999969	0,99997	0,999971	0,999972	0,999973	0,999974	0,999974	0,999975	0,999975
4	0,999975	0,999975	0,999974	0,999974	0,999973	0,999973	0,999972	0,999971	0,99997	0,999968
5	0,999967	0,999965	0,999963	0,999961	0,999959	0,999957	0,999954	0,999952	0,999949	0,999946
6	0,999943	0,99994	0,999936	0,999933	0,999929	0,999925	0,999922	0,999917	0,999913	0,999909
7	0,999904	0,9999	0,999895	0,99989	0,999885	0,999879	0,999874	0,999868	0,999863	0,999857
8	0,999851	0,999845	0,999839	0,999832	0,999826	0,999819	0,999812	0,999805	0,999798	0,999791
9	0,999784	0,999776	0,999768	0,999761	0,999753	0,999745	0,999737	0,999728	0,99972	0,999711
10	0,999702	0,999694	0,999685	0,999675	0,999666	0,999657	0,999647	0,999638	0,999628	0,999618
11	0,999608	0,999598	0,999587	0,999577	0,999566	0,999556	0,999545	0,999534	0,999523	0,999512
12	0,9995	0,999489	0,999477	0,999466	0,999454	0,999442	0,99943	0,999417	0,999405	0,999393
13	0,99938	0,999367	0,999355	0,999342	0,999328	0,999315	0,999302	0,999288	0,999275	0,999261
14	0,999247	0,999233	0,999219	0,999205	0,999191	0,999176	0,999162	0,999147	0,999133	0,999118
15	0,999103	0,999087	0,999072	0,999057	0,999041	0,999026	0,99901	0,998994	0,998978	0,998962
16	0,998946	0,99893	0,998913	0,998897	0,99888	0,998863	0,998847	0,99883	0,998813	0,998795
17	0,998778	0,998761	0,998743	0,998725	0,998708	0,99869	0,998672	0,998654	0,998635	0,998617
18	0,998599	0,99858	0,998561	0,998543	0,998524	0,998505	0,998486	0,998467	0,998447	0,998428
19	0,998408	0,998389	0,998369	0,998349	0,998329	0,998309	0,998289	0,998269	0,998248	0,998228
20	0,998207	0,998186	0,998166	0,998145	0,998124	0,998103	0,998081	0,99806	0,998039	0,998017
21	0,997995	0,997974	0,997952	0,99793	0,997908	0,997886	0,997864	0,997841	0,997819	0,997796
22	0,997773	0,997751	0,997728	0,997705	0,997682	0,997659	0,997635	0,997612	0,997589	0,997565
23	0,997541	0,997518	0,997494	0,99747	0,997446	0,997422	0,997397	0,997373	0,997349	0,997324
24	0,997299	0,997275	0,99725	0,997225	0,9972	0,997175	0,997149	0,997124	0,997099	0,997073
25	0,997048	0,997022	0,996996	0,99697	0,996944	0,996918	0,996892	0,996866	0,996839	0,996813
26	0,996786	0,99676	0,996733	0,996706	0,996679	0,996652	0,996625	0,996598	0,996571	0,996543
27	0,996516	0,996488	0,996461	0,996433	0,996405	0,996377	0,996349	0,996321	0,996293	0,996264
28	0,996236	0,996207	0,996179	0,99615	0,996121	0,996093	0,996064	0,996035	0,996006	0,995976
29	0,995947	0,995918	0,995888	0,995859	0,995829	0,995799	0,99577	0,99574	0,99571	0,99568
30	0,99565	0,99562	0,99559	0,99556	0,99553	0,9955	0,99547	0,99544	0,99541	0,99537
31	0,99534	0,99531	0,99528	0,99525	0,99522	0,99519	0,99516	0,99512	0,99509	0,99506
32	0,99503	0,995	0,99496	0,99493	0,9949	0,99487	0,99484	0,9948	0,99477	0,99474
33	0,9947	0,99467	0,99464	0,99461	0,99457	0,99454	0,99451	0,99447	0,99444	0,99441
34	0,99437	0,99434	0,99431	0,99427	0,99424	0,9942	0,99417	0,99414	0,9941	0,99407
35	0,99403	0,994	0,99396	0,99393	0,9939	0,99386	0,99383	0,99379	0,99376	0,99372
36	0,99369	0,99365	0,99361	0,99358	0,99354	0,99351	0,99347	0,99344	0,9934	0,99337
37	0,99333	0,99329	0,99326	0,99322	0,99319	0,99315	0,99311	0,99308	0,99304	0,993
38	0,99297	0,99293	0,99289	0,99286	0,99282	0,99278	0,99274	0,99271	0,99267	0,99263
39	0,9926	0,99256	0,99252	0,99248	0,99244	0,99241	0,99237	0,99233	0,99229	0,99225

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40	0,99222	0,99218	0,99214	0,9921	0,99206	0,99202	0,99199	0,99195	0,99191	0,99187
41	0,99183	0,99179	0,99175	0,99171	0,99167	0,99163	0,99159	0,99156	0,99152	0,99148
42	0,99144	0,9914	0,99136	0,99132	0,99128	0,99124	0,9912	0,99116	0,99112	0,99108
43	0,99104	0,991	0,99095	0,99091	0,99087	0,99083	0,99079	0,99075	0,99071	0,99067
44	0,99063	0,99059	0,99055	0,9905	0,99046	0,99042	0,99038	0,99034	0,9903	0,99025
45	0,99021	0,99017	0,99013	0,99009	0,99004	0,99	0,98996	0,98992	0,98988	0,98983
46	0,98979	0,98975	0,98971	0,98966	0,98962	0,98958	0,98953	0,98949	0,98945	0,98941
47	0,98936	0,98932	0,98928	0,98923	0,98919	0,98915	0,9891	0,98906	0,98901	0,98897
48	0,98893	0,98888	0,98884	0,98879	0,98875	0,98871	0,98866	0,98862	0,98857	0,98853
49	0,98848	0,98844	0,98839	0,98835	0,98831	0,98826	0,98822	0,98817	0,98813	0,98808
50	0,98804	0,98799	0,98794	0,9879	0,98785	0,98781	0,98776	0,98772	0,98767	0,98763
51	0,98758	0,98753	0,98749	0,98744	0,9874	0,98735	0,9873	0,98726	0,98721	0,98716
52	0,98712	0,98707	0,98702	0,98698	0,98693	0,98688	0,98684	0,98679	0,98674	0,9867
53	0,98665	0,9866	0,98655	0,98651	0,98646	0,98641	0,98636	0,98632	0,98627	0,98622
54	0,98617	0,98613	0,98608	0,98603	0,98598	0,98593	0,98589	0,98584	0,98579	0,98574
55	0,98569	0,98564	0,9856	0,98555	0,9855	0,98545	0,9854	0,98535	0,9853	0,98525
56	0,98521	0,98516	0,98511	0,98506	0,98501	0,98496	0,98491	0,98486	0,98481	0,98476
57	0,98471	0,98466	0,98461	0,98456	0,98451	0,98446	0,98441	0,98436	0,98431	0,98426
58	0,98421	0,98416	0,98411	0,98406	0,98401	0,98396	0,98391	0,98386	0,98381	0,98376
59	0,98371	0,98366	0,98361	0,98355	0,9835	0,98345	0,9834	0,98335	0,9833	0,98325
60	0,9832	0,98314	0,98309	0,98304	0,98299	0,98294	0,98289	0,98283	0,98278	0,98273
61	0,98268	0,98263	0,98257	0,98252	0,98247	0,98242	0,98237	0,98231	0,98226	0,98221
62	0,98216	0,9821	0,98205	0,982	0,98194	0,98189	0,98184	0,98179	0,98173	0,98168
63	0,98163	0,98157	0,98152	0,98147	0,98141	0,98136	0,98131	0,98125	0,9812	0,98115
64	0,98109	0,98104	0,98098	0,98093	0,98088	0,98082	0,98077	0,98071	0,98066	0,98061
65	0,98055	0,9805	0,98044	0,98039	0,98033	0,98028	0,98022	0,98017	0,98011	0,98006
66	0,98	0,97995	0,97989	0,97984	0,97978	0,97973	0,97967	0,97962	0,97956	0,97951
67	0,97945	0,9794	0,97934	0,97929	0,97923	0,97918	0,97912	0,97906	0,97901	0,97895
68	0,9789	0,97884	0,97878	0,97873	0,97867	0,97861	0,97856	0,9785	0,97845	0,97839
69	0,97833	0,97828	0,97822	0,97816	0,97811	0,97805	0,97799	0,97794	0,97788	0,97782
70	0,97776	0,97771	0,97765	0,97759	0,97754	0,97748	0,97742	0,97736	0,97731	0,97725
71	0,97719	0,97713	0,97708	0,97702	0,97696	0,9769	0,97684	0,97679	0,97673	0,97667
72	0,97661	0,97655	0,9765	0,97644	0,97638	0,97632	0,97626	0,9762	0,97614	0,97609
73	0,97603	0,97597	0,97591	0,97585	0,97579	0,97573	0,97567	0,97562	0,97556	0,9755
74	0,97544	0,97538	0,97532	0,97526	0,9752	0,97514	0,97508	0,97502	0,97496	0,9749
75	0,97484	0,97478	0,97472	0,97466	0,9746	0,97454	0,97448	0,97442	0,97436	0,9743
76	0,97424	0,97418	0,97412	0,97406	0,974	0,97394	0,97388	0,97382	0,97376	0,9737
77	0,97364	0,97358	0,97352	0,97345	0,97339	0,97333	0,97327	0,97321	0,97315	0,97309
78	0,97303	0,97297	0,9729	0,97284	0,97278	0,97272	0,97266	0,9726	0,97253	0,97247
79	0,97241	0,97235	0,97229	0,97223	0,97216	0,9721	0,97204	0,97198	0,97191	0,97185
80	0,97179	0,97173	0,97167	0,9716	0,97154	0,97148	0,97142	0,97135	0,97129	0,97123
81	0,97116	0,9711	0,97104	0,97098	0,97091	0,97085	0,97079	0,97072	0,97066	0,9706
82	0,97053	0,97047	0,97041	0,97034	0,97028	0,97022	0,97015	0,97009	0,97003	0,96996
83	0,9699	0,96983	0,96977	0,96971	0,96964	0,96958	0,96951	0,96945	0,96939	0,96932

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84	0,96926	0,96919	0,96913	0,96906	0,969	0,96893	0,96887	0,96881	0,96874	0,96868
85	0,96861	0,96855	0,96848	0,96842	0,96835	0,96829	0,96822	0,96816	0,96809	0,96803
86	0,96796	0,9679	0,96783	0,96776	0,9677	0,96763	0,96757	0,9675	0,96744	0,96737
87	0,96731	0,96724	0,96717	0,96711	0,96704	0,96698	0,96691	0,96684	0,96678	0,96671
88	0,96664	0,96658	0,96651	0,96645	0,96638	0,96631	0,96625	0,96618	0,96611	0,96605
89	0,96598	0,96591	0,96585	0,96578	0,96571	0,96565	0,96558	0,96551	0,96544	0,96538
90	0,96531	0,96524	0,96518	0,96511	0,96504	0,96497	0,96491	0,96484	0,96477	0,9647
91	0,96463	0,96457	0,9645	0,96443	0,96436	0,9643	0,96423	0,96416	0,96409	0,96402
92	0,96396	0,96389	0,96382	0,96375	0,96368	0,96361	0,96355	0,96348	0,96341	0,96334
93	0,96327	0,9632	0,96313	0,96306	0,963	0,96293	0,96286	0,96279	0,96272	0,96265
94	0,96258	0,96251	0,96244	0,96237	0,9623	0,96224	0,96217	0,9621	0,96203	0,96196
95	0,96189	0,96182	0,96175	0,96168	0,96161	0,96154	0,96147	0,9614	0,96133	0,96126
96	0,96119	0,96112	0,96105	0,96098	0,96091	0,96084	0,96077	0,9607	0,96063	0,96056
97	0,96049	0,96042	0,96035	0,96027	0,9602	0,96013	0,96006	0,95999	0,95992	0,95985
98	0,95978	0,95971	0,95964	0,95957	0,95949	0,95942	0,95935	0,95928	0,95921	0,95914
99	0,95907	0,95899	0,95892	0,95885	0,95878	0,95871	0,95864	0,95856	0,95849	0,95842

Table C.1: Density table water. The table lists the density D of water as a function of the temperature under isobaric conditions [24] ***Fehler! Verweisquelle konnte nicht gefunden werden.****: Pure, air-free water H_2O, normal pressure: 1013,25 mbar = 101300 Pa, range: 0 to 99.9°C, density D in g / ml, temperature according to ITS-90 (International Temperature Scale of 1990)*